Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Critical Review of CO$_2$ Separation Technologies for Post Combustion Flue Gases

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Issues With Post-Combustion Flue Gases

- **Unseen Large Scale**
  - *CO$_2$ emission rate (500 MWe PC power plant):*
    500 tonne/hour
    or 4 MM tonnes/year
  - *Flue gas volume:*
    1.6 million standard cubic meter/hour
- **Low product value**
  - *Currently meaningful scale for emission control is Enhanced Oil Recovery (EOR). Other applications are all to small to match magnitude of power plants Energy intensive*

- **Low CO2 concentration**
  - *PC around 10-14 %*
  - *IGCC around 10%*
  - *NGCC 5%*
- **Low (atmospheric) pressure**
  - *Due to huge flue gas volume, it is too expensive to compress to high pressure Table 1 shows the compression work required for a 500 MW power plant*
- **Energy Intensive for CO$_2$ separation**
  - *18 MWe is required minimum separation work.*
  - *Processes need compression will not be attractive*

Power required to compress flue gas for a 500 MW PC power plant

Item	Conditions	Power Requirement
		(MW)
Flue Gas Compression (compressed to 10 atm)	One stage (1 to 10), no cooling	194
	Two stages (1 to 3, 3 to 10), cooling inter-stages	155
	Ideal gas, isothermal compression	145
Power loss due to compression	Assuming a 90% of compressor and expander efficiency	29

Minimum Separation Work

Based on the 2nd law of thermodynamics, minimum separation energy:

$$W_{\min,T} = -RT \left(\sum_j x_{jF} \ln(\gamma_{jF} x_{jF}) - \sum_i \phi_i \sum_j x_{ji} \ln(\gamma_{ji} x_{ji}) \right)$$

Where ϕ_i: molar fraction of product i;

γ_{ji}: activity coefficient of component j in product i;

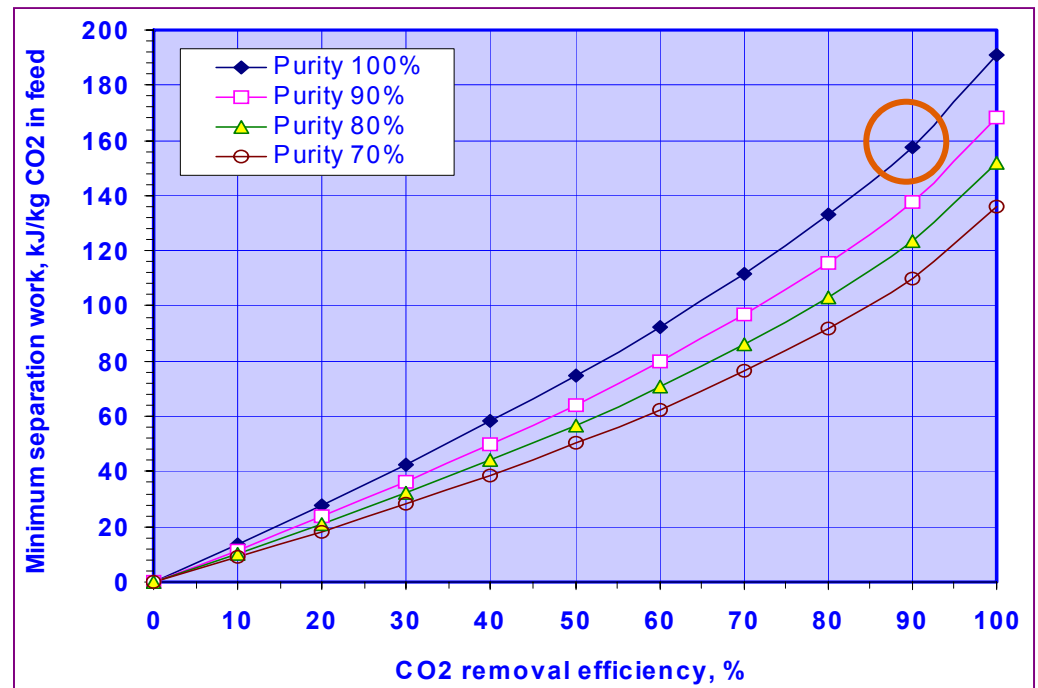X_{ji}: mole fraction of component j in product i;

x_{jF}: mole fraction of component in feed
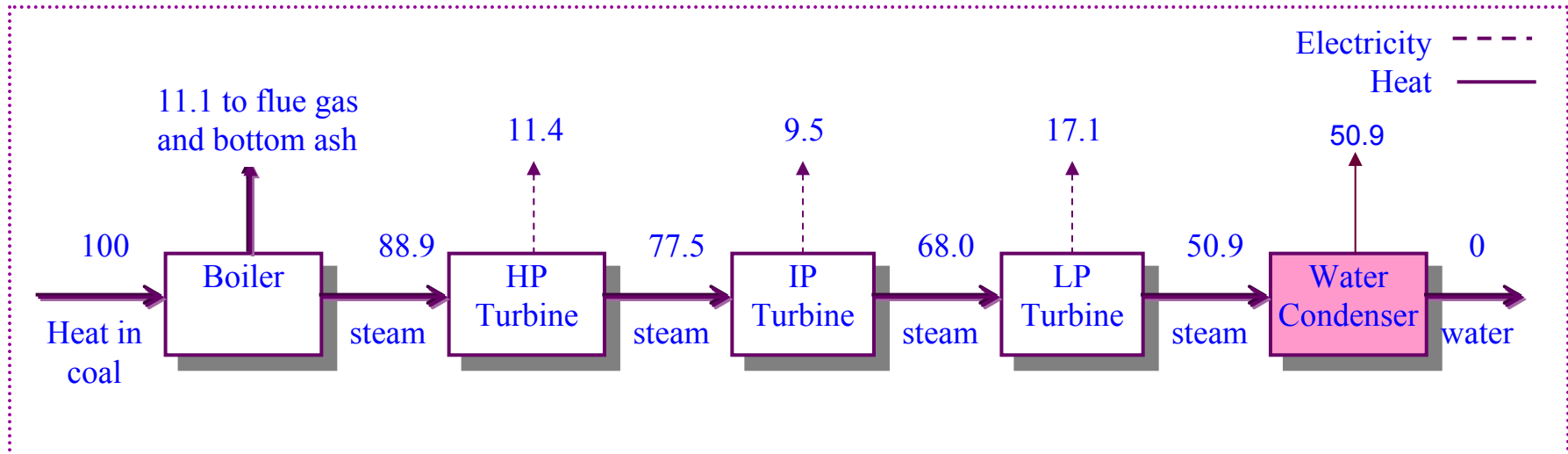
Note:
Minimum separation work is a useful concept for separation processes that only use mechanical work. For separation processes which use heat the concept is not well defined since energy and work are not equal

Minimum separation work for CO_2 separation

Assuming: T=330 K (135 F), 12 vol% CO_2 in flue gas

Energy Flow in a Typical PC power plant

Legend: Electricity - - - -, Heat ——

- Boiler: Heat in coal **100** → steam **88.9**; **11.1 to flue gas and bottom ash**
- HP Turbine: steam **77.5**; **11.4** (electricity)
- IP Turbine: steam **68.0**; **9.5** (electricity)
- LP Turbine: steam **50.9**; **17.1** (electricity)
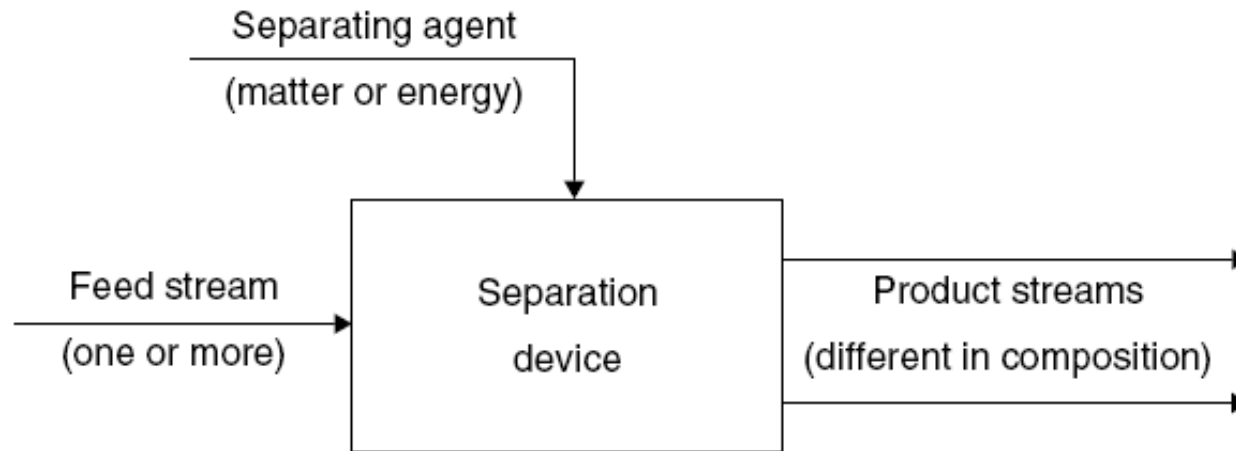- Water Condenser: steam **0**, water; **50.9** (heat)

□ *About 51% of the heat input is released during condensation of the low pressure exhaust steam (1.2 psi, 103 ^{o}F) in the Water Cooling Tower*

□ *Heat within the steam cycle temperature (between 103 to 1000 ^{o}F for PC power plant) has different quality. Higher temperature will have higher potential to produce electricity*

□ *All the heat above the highest temperature in the steam cycle (1000 ^{o}F for PC power plant) will have same quality.*

□ *Any separation process which operates within the steam cycle temperatures (between 103 to 1000 ^{o}F for PC power plant), the one with the lower operating temperature is preferable.*

□ *Any separation process which operates in a temperature range above steam cycle temperature (1000 ^{o}F for PC power plant) will not impact the energy efficiency of the power plant.*

Energy Efficiency of Steam for Electricity Generation
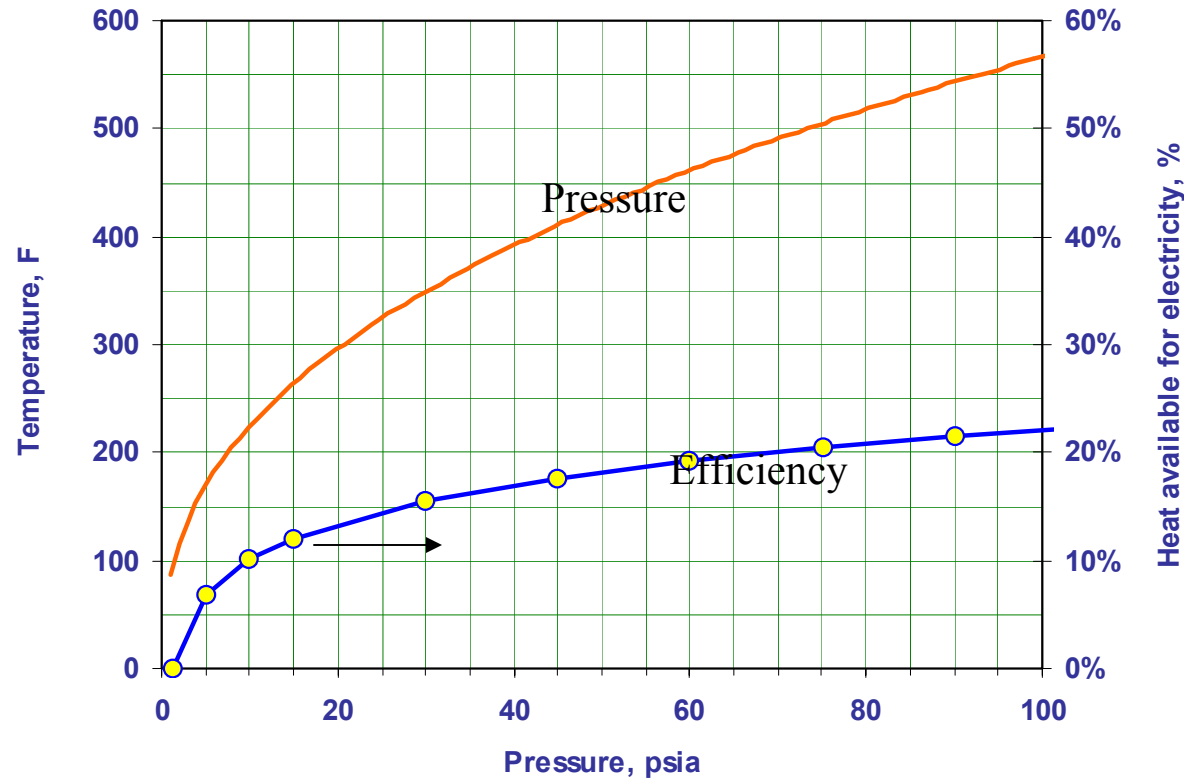
❑ *Steam required in a typical amine base process is around 400 ^oF and has about 20% heat efficiency for electricity*

❑ *If the desorption process can take place at a temperature close to the exhaust steam temperature then the electricity loss due to steam extraction will be minimized*

Typical Separation Process

Separating agent
(matter or energy)

Feed stream
(one or more)

Separation device

Product streams
(different in composition)

Separation processes

➢ **Equilibration processes**
- **Multi-stage in one vessel,**
- **Low separation factor is acceptable**
- **Examples: evaporation, distillation, absorption and liquid extraction**

➢ **Rate-governed processes**
- **One or two stages**
- **Different stage has to be in different separation device**
- **Example: membrane processes**

Separating agent

➢ **Energy: distillation, evaporation**
- **Needs one separation device and usually is the best option for separation processes**

➢ **Matter: absorption, extraction**
- **needs two or more separation devices due to recovery of the matter,**
- **Possible corrosion, contamination, environmental issues**

Absperption Processes

- Is an equilibration process
  - Easily multi-staged (high overall separating factor) if necessary
  - Since can be multi-staged, so high product purity and product recovery can be easily achieved
- Uses mass as separating-agents
  - Two separation devices are required: absorption and desorption
  - Possible corrosion and secondary contamination by the solvent
- Is a gas-liquid system
  - It is easy to handle gas and liquid in continuous operation
  - Operating temperature is limited by the vapor pressure of the solvent and usually is operated at low temperature

- Is a well understood process
  - Industry has gained rich experience and it is easy to scale up the process from bench scale to industrial scale
- Large scale operation
  - Wet FGD processes are large scale absorption processes. The difference is the scales between CO_2 and SO_2 but the flue gas volumes are the same
- Inexpensive equipment
  - Absorption column (such as packed bed) is relative inexpensive to build
- Best option for CO_2 separation from post-combustion flue gases

Absorption Processes

Characteristics of an ideal solvent

- High CO_2 absorption capacity on the per weight solvent bases that can be achieved by using low molecular weigh or increase the stoichiometric ratio (mole ratio of solvent to CO_2)
- Low vapor pressure (high boiling point) of the solvent so that solvent loss and secondary contamination of the flue gas can be prevented
- Low heat of absorption
  - reducing heat of absorption will reduce heat (steam) requirement

- Low $\Delta T = T_{desorption} - T_{absorption}$, which will reduce the sensible heat
- Low operating temperature (low $T_{desorption}$)
  - Will be able to use low quality steam and reduce electricity loss
- Other characteristics:
  - resist to contaminants such as SOx, NOx
  - low cost,
  - no corrosion,
  - non toxic,
  - easy handling

Adsorption Processes

- *Is an equilibration process*
  - *Easily multi-staged (high overall separating factor) if necessary*
  - *Since can be multi-staged, so high product purity and product recovery can be easily achieved*
- *Uses mass-separating-agent*
  - *Two separated steps are required: adsorption and desorption with adsorption to separate CO_2 and desorption to regenerate the mass separating agent*

- *Is a gas-solid system*
  - *Difficult for continuous operation*
- *Operating temperature is limited by the thermal stability of the sorbent*
- *Adsorption is suitable for trace elements removal from bulk gases but not suitable for bulk separation such as CO_2 removal from*
- *Well-understood process and large scale operation is possible unless large amount of heat generation is involved*

Adsorption Processes --Fixed Bed, TSA or PSA

Batch type of fixed bed adsorption process is suitable for trace elements removal, where the sorbent regeneration time is only a small portion of the whole batch cycle time. When the sorbent regeneration time is a large portion of the batch cycle time, the economic performance of the adsorption process will be strongly impacted.

The table below shows the results for a 500 MW power plant with CO_2 emission rate of 500 metric tonnes/hour. It is also assumed that sobent capacity usage in the adsorption column is 80%.

❑ *Note: pure VSA is not practical if high CO_2 recovery is desired due to the pressure drop along the adsorption column*

Number of adsorption columns required for adsorption processes for a 500 MW PC power plant

| Operating Configuration	Column diameter (m)	Height (m)	Capacity (gCO$_2$/g sorbent)	Cycle time (hour)	Sorbent Packing Density (g/cm^3)	# of Column required
Fixed bed TSA	3.1	32	0.1	2	0.8	58
PSA and VSA	3.1	32	0.1	0.4	0.8	12

Fluidized bed Adsorption

Circulated fluidized bed or entrained bed

Fluidized bed is the only possible configuration for adsorption process.

The potential problems are:

❑ *It operates co-currently which will reduce mass transfer driving force and increase energy consumption*

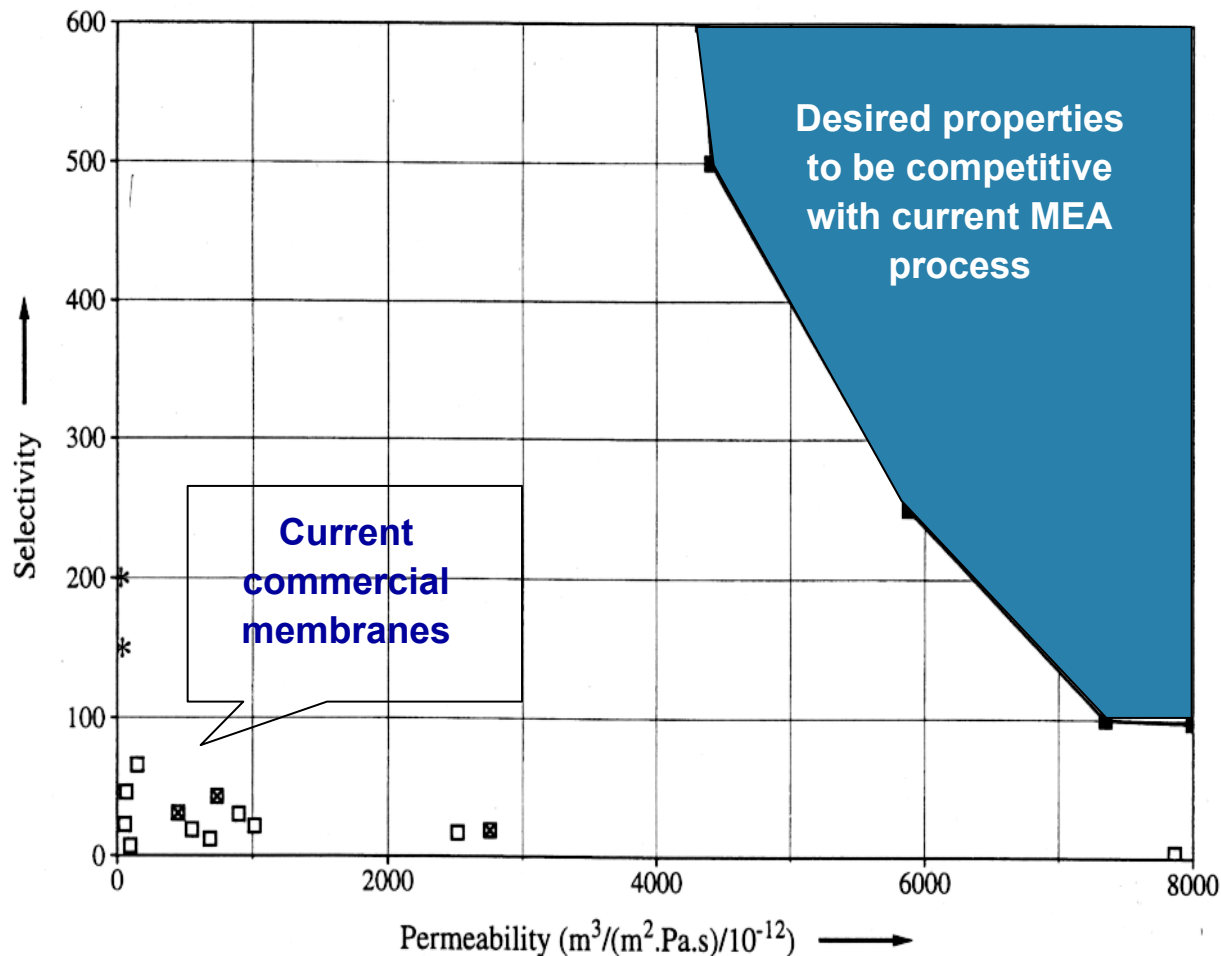❑ *Attrition of the sorbent*
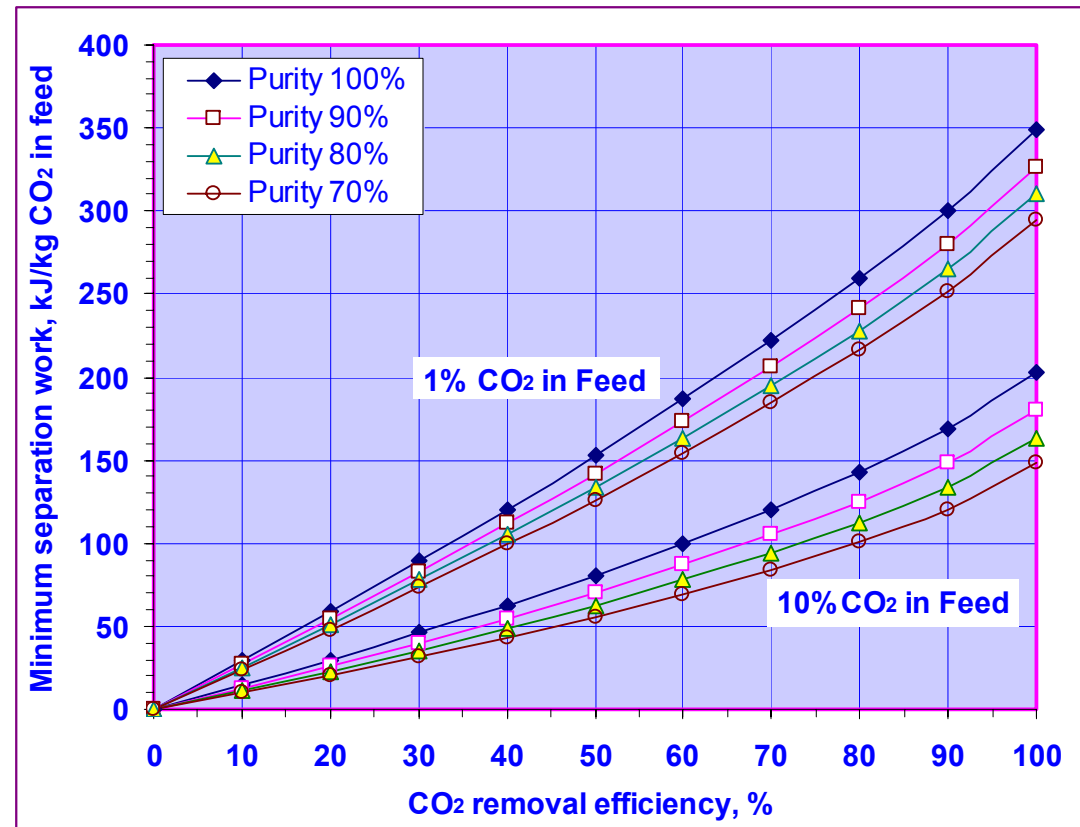
Minimum separation work will increase when the co-current configuration is used (assuming a 90% recovery rate)

Membrane Separation Process

- Is a rate-governed process
  - Usually is one or two staged
  - Requires a high selectivity
  - Trade off between product purity and product recovery rate
- Use energy as separating-agent
  - Pressure is the separation driving force
  - Compression of the feed gas is needed to achieve higher recovery rate
- Gas or liquid (usually one phase system)
  - easy for continuous operation
- Operating temperature is determined by the membrane thermal stability
  - High temperature is possible
- Requires gas pre-treatment (liquid, mist, particulates, trace contaminants, heating)

- Advantages:
  - Compact equipment size
  - Easy to scale up due to its module nature
  - Little maintenance
- Disadvantages
  - Expensive equipment cost
  - Low recovery rate
  - Often requires pre-treatment
  - To produce pipeline transportation ready CO_2 will reduce recovery rate
  - Needs compression
  - Energy intensive
    - A one-staged membrane process with 90% CO_2 recovery requires minimum separation work of around 36MWe

Membrane Separation Process

Current economic performance of membrane separation process and its required quality to compete with current MEA processes
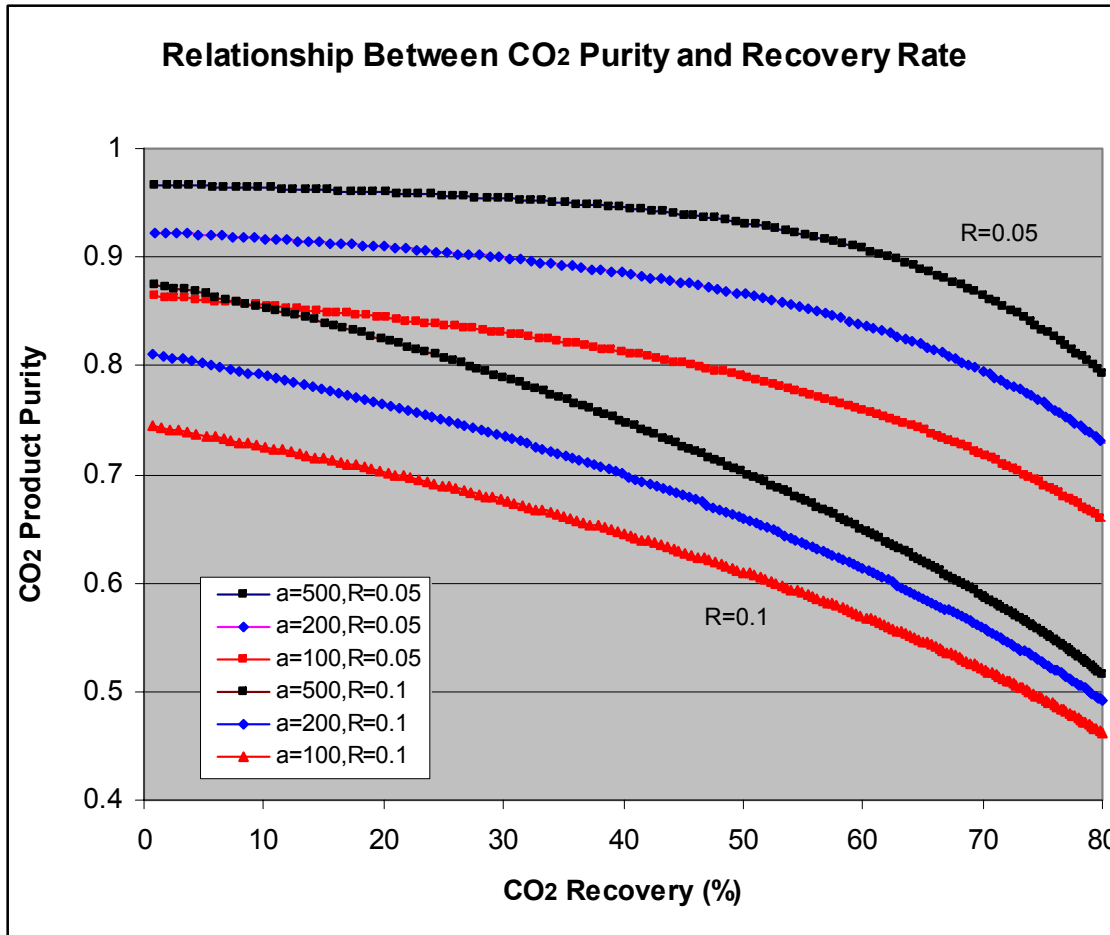
Note:

- *Current MEA process is still too expensive and needs to be improved*

- *Selectivity and permeability of a membrane is often reversely correlated. Very difficult to increase both at the same time*

Membrane Technology

Relationship Between CO₂ Purity and Recovery Rate

Legend:
- a=500,R=0.05
- a=200,R=0.05
- a=100,R=0.05
- a=500,R=0.1
- a=200,R=0.1
- a=100,R=0.1

R=0.05

R=0.1

X-axis: CO₂ Recovery (%)
Y-axis: CO₂ Product Purity

Trade-off between product purity and product recovery rate for a single staged membrane separation process

In the Figure: a is the selectivity (CO_2/N_2) of the membrane and R is the pressure ratio between retentate side and permeate side

Note: for pipeline transportation the CO_2 purity is at least 95%. Obviously, the recovery rate will be very low unless a second stage is added, which will increase the compression work

Cryogenic Process

- Is an equilibration process
  - Easily be operated in multi-staged mode (high overall separation factor)
  - High product purity and high product recovery can be easily achieved
- Uses energy as separating-agent
  - Only one separating devise is required
- Is a vapor-liquid system
  - easy for continuous operation
  - Process has to be operated in vapor-liquid zone of the phase diagram
- Operating temperature is limited by the volatility of all the flue gas components combined

Advantages
- Product CO_2 is in liquid state and needs no further compression
- High purity CO_2 and is pipeline transportation ready
- High recovery rate

Disadvantages
- The lowest pressure required to recover any CO_2 is around 50 bar and at a temperature of around -57 C. To recover 90% of CO_2, as high as 347 bar pressure may be needed
- Power loss due to the compression and expanding (to recover compression work) of the flue gas will very high
- All the water in the flue gas has to be removed to prevent the blockage of the system

Cryogenic Process

Cryogenic process has to be operated in the vapor-liquid phase zone between the triple point and the critical point and the flue gas conditions have to be changed from point ❶ *to* ❷ *in the figure*
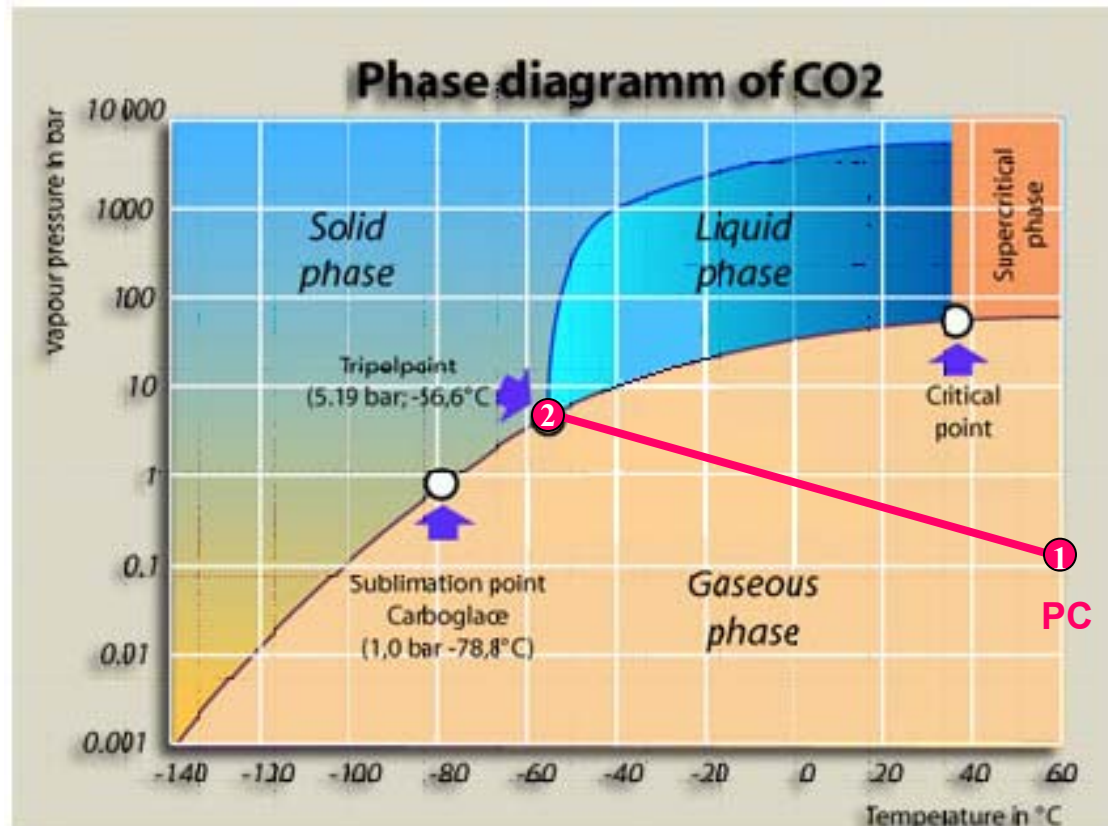
PC plant:
❶   *Flue gas: P_{CO_2} = 0.10 Bar, P=1 Bar, 60 ºC*
❷   *lowest pressure to reach vapor-liquid zone will be close to -57 ºC and 50 Bar*

Conclusions

- *Any separation processes that need compression of the flue gas will not be attractive*
- *Absorption processes*
  - *Best options for post-combustion CO_2 separation*
- *Adsorption processes*
  - *Fixed bed configuration is unpractical*
  - *PSA and VSA process are unlikely*
  - *Fluidized bed is the only configuration*

- *Membrane process*
  - *Uses high pressure operation is unpractical*
  - *Use vacuum at the permeate side is the best option*
  - *Increase the permeability is the key*
  - *absorption/membrane Hybrid process*
- *Cryogenic process*
  - *Needs high pressure and low temperature*
  - *Not practical for CO_2 separation from post-combustion flue gases*